

A phase-separation perspective on dynamic heterogeneities in glass-forming liquids

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We study dynamic heterogeneities in a model glass-former whose overlap with a reference configuration is constrained to a fixed value. The system phase-separates into regions of small and large overlap, so that dynamical correlations remain strong even for asymptotic times. We calculate an appropriate thermodynamic potential and find evidence of a Maxwell’s construction consistent with a spinodal decomposition of two phases. Our results suggest that dynamic heterogeneities are the expression of an ephemeral phase-separating regime ruled by a finite surface tension.

The conspicuous lack of a growing correlation length, contrasting with the very steep increase of the relaxation time, has been a puzzle in the physics of structural glasses for quite a long time. Arguably, the first breakthrough has been the discovery of dynamic heterogeneities [1], and the detection of a growing dynamical correlation length, ξ_d [2, 3]. If we take two snapshots of the system separated by a time lag comparable to the α relaxation time, τ_α , the particle displacements vary enormously across the system, and the typical size ξ_d of the mobility-correlated regions increases on lowering the temperature.

More recently, by studying the thermodynamics of systems subject to amorphous boundary conditions [4, 5], an entirely different, fully static, correlation length ξ_s has been discovered [6, 7]. ξ_s also grows upon cooling, even though its surge occurs at lower temperatures than ξ_d . The static correlation length has a natural interpretation as the size of the cooperatively rearranging regions [8], and within the random first-order theory [9] it is determined by the balance between a surface tension cost and a configurational entropy gain of a rearrangement.

Clearly, it would be desirable to unify the dynamic and the thermodynamic frameworks, so as to understand the interplay between the two correlation lengths. Although the static-dynamic connection is clear in mean-field systems [10] and some progresses have been made in more realistic systems [11], we are quite far from a unifying picture in real glass-formers. Here we show that surface tension, which is a crucial ingredient of the thermodynamic framework, also plays a key role in the formation

of dynamic heterogeneities. In so doing, we establish a much-needed further link between dynamic and thermodynamic relaxation in glass-forming liquids.

Let us start with the standard measurement of the dynamic correlation length ξ_d . Our glass-former is the well-known soft-sphere model in 3- d [26]. A useful tool to measure ξ_d is the overlap, which quantifies how much a configuration at time t is similar to the reference configuration at $t = 0$. If we partition the system in small cubic boxes and let n_i be the number of particles in box i , the local overlap is defined as $q(\mathbf{r}_i, t) \equiv n_i(t) n_i(0)$, where \mathbf{r}_i refers to the centre of cell i [27]. The spatial map of the local overlap tells us how much different regions of the system have decorrelated (respect to the initial configuration) over a time t . In Fig. 1 (top) we show two snapshots of the overlap field. We see that at $t = \tau_\alpha$ there are large heterogeneous regions, which eventually fade away for longer times. To quantify their size we must compute the overlap correlation function,

$$G(\mathbf{r}, t) \equiv \langle q(0, t) q(\mathbf{r}, t) \rangle - \langle q(0, t) \rangle \langle q(\mathbf{r}, t) \rangle, \quad (1)$$

or its Fourier transform $S(k, t)$ (Fig. 2, left). In general, given a correlation function in Fourier space, it is well-established practice [12] to extract the correlation length ξ from the small- k linear interpolation of S^{-1} vs. k^2 ,

$$S(k, t)^{-1} = A + Bk^2, \quad (2)$$

from which the correlation length is obtained as $\xi(t)^2 = B/A$. The validity of Eq. 2 is shown in the inset of Fig. 2, right. [28]. The time-dependent correlation length $\xi(t)$ represents the size of the dynamical heterogeneities at time t . This lengthscale grows as the time approaches τ_α and the heterogeneities become more extended (inset of Fig. 2, left). The largest value of $\xi(t)$ (reached at the τ_α) defines the so-called dynamical correlation length, $\xi_d \equiv \xi(\tau_\alpha)$ [2, 3, 13].

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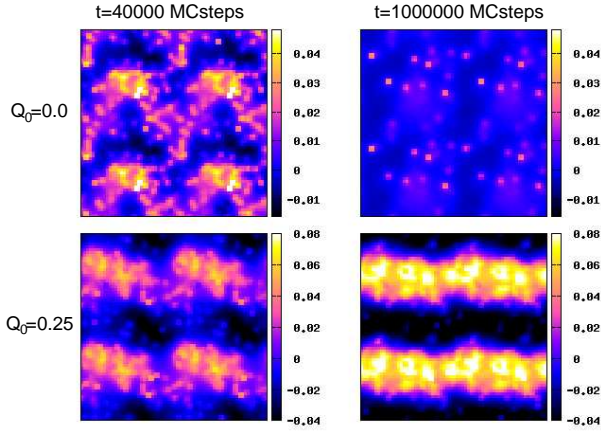


FIG. 1: Fluctuations of the overlap field, $\delta q(\mathbf{r}, t) = q(\mathbf{r}, t) - \langle q(t) \rangle$ for a 2-d slice of the system. Upper panels: unconstrained system. Lower panels: constrained system ($\hat{Q} = 0.25$). Left panels: $t = \tau_\alpha$. Right panels: large times. $L = 16$.

What happens beyond τ_α ? The memory of the initial configuration is gradually lost, so that the correlation function $S(k, t)$ decays sharply, Fig. 2 (left). What happens to $\xi(t)$ is less clear, because the vanishing of $S(k, t)$ makes it hard to fit a reliable value of $\xi(t)$ through Eq. 2. Although this point is debated [14], our results indicate that $\xi(t)$ decreases beyond τ_α (left inset of Fig. 2), in line with other studies [13]. However, what is important, and definitely out of question, is that the *correlation* decreases for large times, irrespective of its spatial range. Heterogeneities blur as $q(\mathbf{r}, t)$ becomes zero everywhere, and their size $\xi(t)$ becomes somewhat ill-defined.

Let us now make a different experiment. We want to impose a constraint on the dynamics, so that the system cannot entirely lose memory of its initial configuration. This can be implemented by imposing a lower bound on the global overlap, $Q(t) = 1/V \int d\mathbf{r} q(\mathbf{r}, t)$. In the unconstrained case $Q(t)$ goes asymptotically to zero, as the memory of the initial configuration fades [29]. On the other hand, if we run the dynamics with the constraint $Q(t) \geq \hat{Q}$ things change [30]. Initially the system does not feel the constraint: the global overlap decreases from its $t = 0$ value, $Q = 1$, and everything proceeds as described above, including the growth of the heterogeneities. However, at later times $Q(t)$ hits its lower bound \hat{Q} and it cannot decrease further. What happens to the dynamical heterogeneities in this case?

There are two alternative hypotheses. First, the correlation $S(k, t)$ and its spatial range $\xi(t)$ decay to zero for large t as in the free case. Due to the constraint, however, such endgame cannot happen in the same manner as in the free case, i.e. with $q(\mathbf{r}, t)$ becoming zero everywhere. Heterogeneities must thus become very small, forming a salt-and-pepper configuration of the field $q(\mathbf{r}, t)$, so that the total integral of the field stays equal to \hat{Q} . Yet,

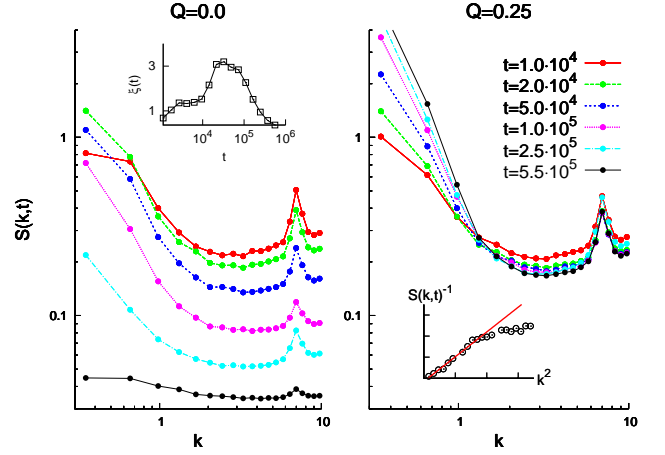


FIG. 2: $S(k, t)$ at different times for the unconstrained (left) and constrained (right, ($\hat{Q} = 0.25$)) cases. Left inset: correlation length $\xi(t)$ as extracted from Eq. (2). Right inset: $S(k, t)^{-1}$ vs. k^2 . $T = T_{MC}$ and $L = 16$.

if there is a nonzero surface tension between high and low overlap regions, such a scenario is not what we expect: the surface tension would force different domains to merge, driving the system towards a phase-separated, highly correlated state [15]. Hence, the second hypothesis is that the correlation *does not* decay and that the dynamic correlation length $\xi(t)$ grows beyond ξ_d , up to an asymptotic value of the order of the system's size L . The stark difference between these two hypotheses suggests that the constrained experiment may clarify the mechanisms of formation of dynamical heterogeneities.

Inspection of the overlap field in the constrained case, Fig. 1 (bottom), is quite telling: for large t the system phase separates into high and low overlap regions, forming stable dynamical heterogeneities of the order of the system size. From a quantitative point of view the situation is equally clear: in contrast with the free case, the constrained correlation does not go to zero for large times, but saturates at a finite value, Fig. 2 (right). Hence, even in the late time regime dynamic heterogeneities remain strongly correlated.

The study of the correlation length in the constrained case confirms this scenario [31]. In an infinite system undergoing phase separation, or at a critical point, the intercept A in Eq. 2 vanishes while the slope B remains finite, so that ξ grows indefinitely [12]. On the other hand, in a *finite* system phase separation means that ξ becomes comparable with system size L . As a consequence, the finite-size (periodic) real space correlation function $G(\mathbf{r}, t)$ ceases to be a simple exponential for large r (small k). This implies that the intercept A in Eq. 2 can go below zero and take small negative values ($O(1/L^2)$). In a finite-size system it is therefore convenient to compare $A/B = \xi^{-2}$ vs. L^{-2} to check whether or not phase separation occurs. From Fig. 3 (left) we see that in the

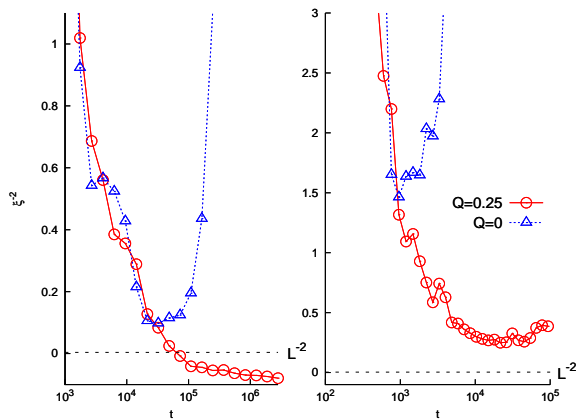


FIG. 3: Left: $A/B = \xi^{-2}(t)$ (see Eq. 2) at $T = T_{MC}$ in the constrained (circles) and unconstrained (triangle) cases. Right: the same at $T = 1.55T_{MC}$. $L = 16$.

unconstrained case ξ^{-2} keeps well clear of L^{-2} , while in the constrained case $\xi^{-2}(t)$ unmistakably goes below L^{-2} . This is exactly what we expect in a system with nonzero surface tension undergoing phase separation. We studied two other sizes, $L = 8$ and $L = 25$, and in both cases $\xi^{-2}(t)$ drops below L^{-2} , indicating phase separation. At higher temperatures, however, though the correlation is enhanced by the constraint, the latter is ineffective to make $\xi^{-2}(t)$ drop below L^{-2} (Fig. 3, right). These results are consistent with the idea that the surface tension decays at high temperature, thus preventing phase separation [16].

In systems with conserved order parameter undergoing phase separation the domains size $\xi(t)$ grows as $t^{1/3}$ and the dynamics proceeds by reducing the total amount of interfaces, and therefore of energy, in the system [15]. The interface energy per domain scales like ξ^θ , where θ is the surface tension exponent. The total number of domains is L^d/ξ^d , so that the total interface energy density is $\Delta E(t) \sim 1/\xi(t)^{d-\theta} \sim 1/t^{(d-\theta)/3}$. In the standard case $\theta = d - 1$, so that $\Delta E(t) \sim 1/t^{1/3}$ [15]. Fig.4 shows that something remarkably similar happens in our case. After the constraint kicks in, $\Delta E(t)$ decays compatibly with an exponent $1/3$. Hence, even though fitting coarsening exponents is notoriously difficult, and one must be careful in drawing any conclusion, our data seems to be compatible with the ‘naive’ exponent $\theta = 2$ [16, 17].

In general, phase-separation is the landmark of first order phase transitions and metastability. At the mean-field level one can normally define a thermodynamic potential as a function of the order parameter that, below some spinodal point, exhibits a stable and a metastable minimum, corresponding to the two phases. In finite dimension Maxwell’s construction makes the potential convex, so that the derivative of the potential is constant (zero second derivative) in a finite interval (Fig. 5, inset). Maxwell’s construction implies that when the order

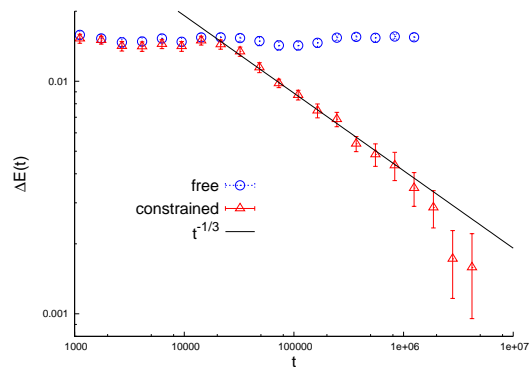


FIG. 4: Energy difference $\Delta E(t) = E(t) - E_0$ vs t at $T = T_{MC}$ with constrained dynamics, $\hat{Q} = 0.25$. E_0 is a parameter of the fit $E(t) = E_0 + \gamma t^{-1/3}$. The line is $1/t^{1/3}$, corresponding to the surface tension exponent $\theta = 2$.

parameter is conserved and constrained to take a value in the non-convex interval, phase separation occurs. We have clearly observed phase-separation. Can we define a thermodynamic potential displaying Maxwell’s construction?

Let us proceed minimalistically. Our phase-separating order parameter is the overlap Q , so it is a potential $W(Q)$ we are after. Besides, the potential must determine the observed probability distribution of Q through the relation, $P(Q) = \exp[-NW(Q)] \theta(Q - \hat{Q})$, where the θ -function enforces the constraint [18]. If we compute the average linear fluctuation of Q and expand the exponential, we obtain,

$$W'(\hat{Q}) \sim N^{-1} \langle Q - \hat{Q} \rangle^{-1}. \quad (3)$$

This quantity is easy to compute: we let the system evolve until the constraint is hit, and then we measure the (very small) average fluctuation of the overlap Q over \hat{Q} (see [19] for a different definition of the potential). We report $W'(\hat{Q})$ in Fig.(5). The second derivative of the potential is clearly nonzero at high T , whereas around the Mode Coupling temperature a finite region with $W''(\hat{Q}) \sim 0$ develops. This is evidence of Maxwell’s construction and it supports the link between phase separation and metastability in our system.

$W(Q)$ is a finite-dimensional variant of the two-replica potential originally introduced in mean-field spin-glasses [20], and later generalized to structural glasses [21]. This potential is the free energy cost to keep a configuration (the running one in the present work) at fixed overlap Q with a generic equilibrium configuration (the initial reference one). Below a dynamic transition (roughly, the Mode Coupling temperature), the mean-field potential develops a metastable minimum at a finite value of Q . In this framework relaxation at low temperatures can be interpreted as a barrier crossing process, bringing the system from the metastable minimum (short times, finite Q) to the stable minimum (long times, zero Q) [22]. The

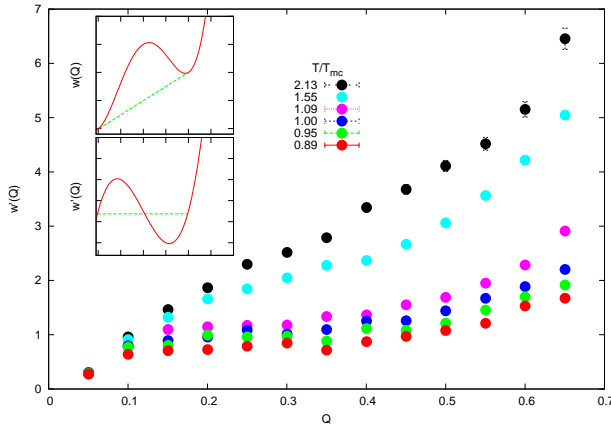


FIG. 5: The derivative $W'(\hat{Q})$ of the thermodynamic potential at different temperatures, ranging from $2.13T_{MC}$ to $0.89T_{MC}$. Inset: a cartoon of Maxwell's construction for the potential and its derivative.

constraint is just a stratagem to keep the overlap within the nonconvex region of the potential, as to interrupt relaxation and therefore force phase separation.

We have studied dynamic heterogeneities in a glass-forming liquid with constrained global overlap. At low temperature both the dynamic correlation function and the thermodynamic potential indicate that the system phase separates into regions of high and low overlap. On the contrary, at high temperature no phase separation occurs, supporting the view of a surface tension that decreases at high T . The co-existence of regions belonging to different amorphous ‘states’ (here the high/low overlap patches) is reminiscent of the random first-order theory of thermodynamic relaxation [9]. In the dynamical case the evolution of these regions is driven by a classic coarsening mechanism, which is stable with the constraint, but ephemeral in absence of the constraint. In the thermodynamic case, on the other hand, the evolution of these regions is presumably driven by an entropic mechanism [9]. Our results show that surface tension and metastability stand as key links between the two frameworks.

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- [26] We simulate the 3-*d* soft-sphere binary mixture [23] with parameters as in ref. 7. Simulations were done with Metropolis Monte Carlo with particle swaps [24]. The mode-coupling temperature for this system is $T_{MC} = 0.226$ [25]. Our largest system has $N = 16384$ particles in a box of length $L = 25.4$.
- [27] The side ℓ of the cells is such that the probability of finding more than one particle in a single box is negligible.
- [28] The so-called *second-moment* correlation length is obtained by computing A and B using only the first two points, $\xi^2 = [S^{-1}(k_1)/S^{-1}(0) - 1]/k_1^2$, where $k_1 = 2\pi/L$ [12]. However, we find that a linear fit to a few small- k points gives equivalent results for ξ^2 yet lowering statistical errors. Of course, the free-field form (2) of $S(k, t)$ does not hold at generic values of k .
- [29] Actually, normalization is such that $Q = \ell^3 = 0.062876$ for completely uncorrelated configurations, while $Q = 1$ for two identical configurations.
- [30] To enforce the constraint we modify the Metropolis algorithm: the probability to accept a move is $p = \min\{1, \exp^{-\Delta E/T}\}$ for $Q(t) \geq \hat{Q}$, and $p = 0$ for $Q(t) < \hat{Q}$.
- [31] Due to the constraint, the space integral of the correlation function is zero, hence the single point $S^{-1}(0, t) = [\int d\mathbf{r} G(\mathbf{r}, t)]^{-1}$ must be excluded from the analysis. This also implies that the dynamical susceptibility, $\chi(t) = S(0, t) = V[\langle Q^2(t) \rangle - \langle Q(t) \rangle^2]$, a standard marker of heterogeneous dynamics, is trivially zero and therefore useless with the constraint.